Canada

PHOTOCHEMISTRY
OF SMALL MOLECULES

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National Bureau of Standards

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Preface

This book has been written in an attempt to cover the remarkable progress made in recent years in the field of photochemistry of small molecules with up to five atoms in the gas phase.

The advancement of flash photolysis–kinetic spectroscopy, laser technology, and other new techniques has made possible the detection of photochemical primary products and detailed studies of photodissociation dynamics. The secondary processes of atoms and radicals formed in the primary process have also been studied extensively. The reactivities of electronically excited atoms (C, O, S, etc.) and radicals (C_2O, CH_2, etc.) have been found to be very different from those of corresponding ground state atoms and radicals. The results of these studies, together with the traditional end product analysis and quantum yield measurements, have greatly aided in our understanding of the photochemical processes, particularly for small molecules. These recent developments, as well as the underlying principles, are described in some detail in dealing with the photochemistry of about 80 small molecules.

Studies of the photochemical processes of small molecules are not only of intrinsic interest but also are important in understanding the photochemistry of isotope enrichment, of air pollution in the troposphere and stratosphere, and of the atmospheres of other planets.

This book is aimed at the physical chemist, spectroscopist, and atmospheric scientist interested in photochemistry. As a reference book it lists about 1200 papers, including some original classic studies and those of recent years up to July 1977. The space limitation and the tremendous amount of publication in the last decade have prevented inclusion of some important papers. I apologize to those whose work has not been quoted.

Since the photochemical reaction is initiated by absorption of light in the visible, ultraviolet, and vacuum ultraviolet regions, an understanding of atomic and molecular spectroscopy is required. *Chapter I* gives a brief introduction to the electronic states and transitions in atoms and simple molecules.

The primary photochemical process brought about by light absorption is dealt with in *Chapter II*. A great deal of information on photodissociation dynamics (such as the lifetimes of the excited states of reactant molecules and the electronic, translational, and internal energy distribution in photofragments) has recently been obtained, particularly for some diatomic and

triatomic molecules. Quantum mechanical theory dealing with dynamics of photodissociation has been proposed by many workers.

Various experimental techniques of photochemistry are described briefly in *Chapter III*.

Further details are given by Calvert and Pitts (4), Noyes and Leighton (22), and McNesby et al. (685a).

Production, detection, and reactivities of various electronically excited atoms are given in *Chapter IV*. The importance of electronically excited atom reactions in photochemistry has been recognized only recently.

Photochemical processes and electronic states of simple molecules with up to five atoms and radicals with up to four atoms in the gas phase are covered in *Chapters V through VII*. The absorption coefficients available for many molecules are shown in figures, as they are important in understanding the quantitative aspect of photochemistry. Bond dissociation energies given are calculated mostly from enthalpies of formation of atoms, radicals, and molecules tabulated in the *Appendix*.

Finally, enrichment of isotopic species has been achieved for a number of atoms and molecules using an appropriate monochromatic light source that preferentially excites an isotopic species of interest in mixtures of other isotopic species. The photochemistry associated with isotopic enrichment is briefly described in *Chapter VIII*. Great efforts have been made recently to obtain information on the detailed photochemical processes involving smog formation, stratospheric pollution, and atmospheres of other planets, and brief discussions of these subjects are also presented in the chapter.

I would like to express my appreciation to Professor W. A. Noyes, Jr., who introduced me to the field of photochemistry and to the late Dr. E. W. R. Steacie, the late Professor W. Groth, and Professor J. R. McNesby, who taught me various aspects of photochemistry. I am particularly grateful to Dr. R. E. Rebbert who has carefully read Chapters I, II, and VII and to Dr. A. H. Laufer for his critical reading of Chapters III through VI and VIII. Their numerous suggestions have greatly improved the manuscript. Thanks are due to Dr. M. D. Scheer for his continuous encouragement and to many friends and colleagues, especially to Drs. D. Garvin, P. J. Ausloos, R. F. Hampson, M. Krauss, and V. H. Dibeler and Professor J. P. Simons for their help and discussion during the preparation of the manuscript. I would like to thank Professor S. A. Rice at the University of Chicago who has given me the opportunity to write this book. I am indebted to Mrs. P. A. Davis who did an excellent job in typing the entire manuscript.

Hideo Okabe

Gaithersburg, Maryland
March 1978

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CHAPTER VII: PHOTOCHEMISTRY OF POLYATOMIC MOLECULES

FOUR-ATOM MOLECULES

FIVE-ATOM MOLECULES

PHOTOCHEMISTRY OF SMALL MOLECULES

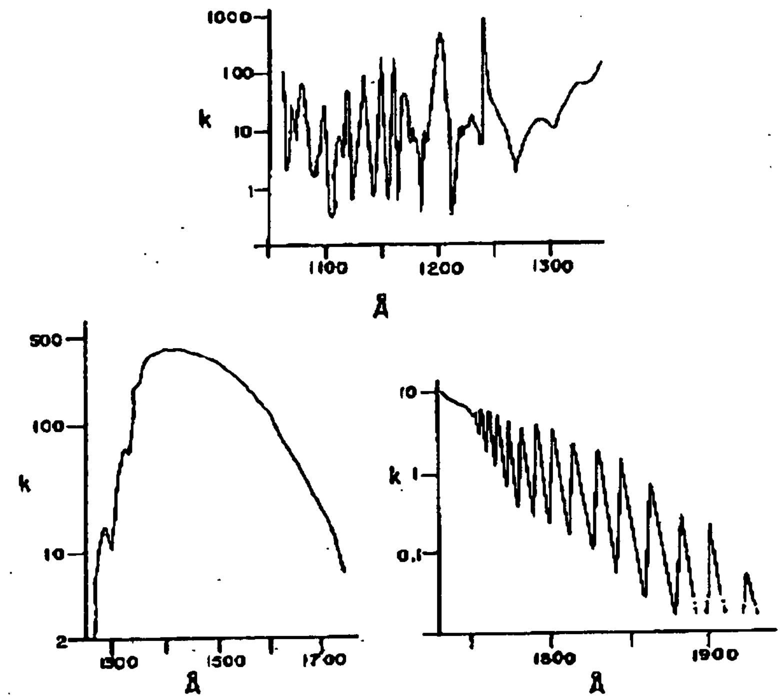

Fig. V–12. Absorption coefficients of O_2 in the region 1100 to 2000 Å. k is in units of $atm^{-1}\ cm^{-1}$, 0°C, base e. 1300 to 1700 Å, Schumann-Runge continuum. 1750 to 1950 Å, Schumann-Runge bands. From Watanabe et al. (1014), reprinted by permission. Copyright 1953 by the American Institute of Physics.

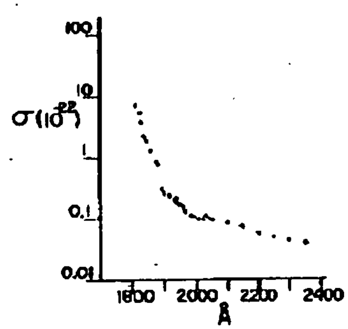

Fig. V–13. The absorption cross sections of the O_2 continuum in the 1814 to 2350 Å region. σ is in units of $10^{-22}\ cm^2\ molec^{-1}$, base e, at room temperature. The absorption cross sections are measured at minima between the well-separated rotational lines of the Schumann-Runge bands for $\lambda < 2025$ Å. σ increases with pressure probably as a result of the formation of O_4. The data are values at the low pressure limit. From Ogawa (755), reprinted by permission. Copyright 1971 by the American Institute of Physics.

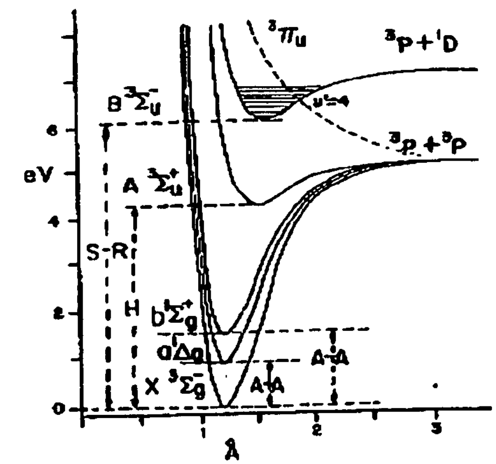

Fig. V–14. Potential energy curves of O_2. S-R, Schumann-Runge bands; H, Herzberg bands; A-A, atmospheric bands. The line-broadening was observed at $v' = 4$ of the $B^3\Sigma_u^-$ state at which point the repulsive $^3\Pi_u$ state crosses the $B^3\Sigma_u^-$ state. See Murrell and Taylor (726). From "Dissociation Energies and the Spectra of Diatomic Molecules" by Gaydon, 3rd Ed. 1968, p. 74, reprinted by permission of Associated Book Publishers Ltd.

determined (104, 341, 444). They are given in Table V–8. Ackerman et al. (38) have measured the absorption coefficients for individual rotational lines in the region 1750 to 2050 Å. The oscillator strengths of the Herzberg I bands from (4, 0) to (11, 0) have been measured by Hasson and Nicholls (446). An absorption coefficient of $0.30 \pm 0.03\ atm^{-1}\ cm^{-1}$ at the 1216 Å line has been determined by several workers (381, 753).

Photochemistry. The threshold wavelengths for the production of $O(^3P)$, $O(^1D)$, and $O(^1S)$ are given below.

	Threshold Wavelength (Å)
$O_2 \xrightarrow{h\nu} O(^3P) + O(^3P)$	2424
$O_2 \xrightarrow{h\nu} O(^3P) + O(^1D)$	1750
$O_2 \xrightarrow{h\nu} O(^3P) + O(^1S)$	1332

Ackerman and Biaume (37) have observed that rotational lines become diffuse at $v' = 4$, 8, and 11 for the Schumann-Runge system. They attribute the diffuseness to predissociation.

A line width of $3\ cm^{-1}$ observed by them implies a lifetime on the order of 10^{-11} sec for the (4, 0) level. It is suggested by Carroll (192) and Murrell and Taylor (726) that predissociation is due to the crossing of the repulsive